

## Using Detailed Chemical Composition of Surfaced Oil to Inform History and Predict Aerosol Formation: Insights on Subsurface Oil Transport and SOA yields from Intermediate Volatility Organic Compounds

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Releases of hydrocarbons from oil spills can have large environmental impacts in both the ocean and atmosphere. While evaporation of oil following a spill is mainly modeled simply as a mass loss mechanism, the resulting production of atmospheric pollutants can also be a major concern, particularly for continental releases, such as wrecks of river barges or train tankers near population centers. Following on observations of significant secondary organic aerosol (SOA) production from the Deepwater Horizon (DWH) spill, we modeled oil evaporation and the resulting potential SOA formation. Composition of surfaced oil indicates multiple transport pathways after release, and comparison of modeled SOA to observations of SOA during the DWH spill suggest high and rapid yields of SOA from intermediate volatility organic compounds (IVOC). Oil-spill conditions (e.g. sea-surface vs. sea-floor release) also affect the rate of evaporation and composition of oil-spill vapor plumes and pollutant formation.

Novel bottom-up modeling of oil evaporation is based on unprecedented characterization of oil composition from the *Deepwater Horizon (DWH)* oil spill using GC×GC-VUV-HRTOFMS. Complete characterization was achieved for GC-amenable compounds from C10-C30 according to degree of branching, number of cyclic rings, aromatic character, and molecular weight. Such detailed and comprehensive characterization of the *DWH* oil allows for bottom-up estimates of the relationship between oil volatility and composition. We developed an evaporative model, based solely on our composition measurements and thermodynamic, rather than common boiling point parameterizations, which is in excellent agreement with published mass evaporation rates. Measured oil volatility distributions were different than previously estimated, suggesting accurate SOA prediction requires detailed oil composition measurements. Supporting experiments in a wind tunnel verify model accuracy and show that the relative mass transfer of individual components depends on slick thickness and evaporation rate.

With modeled evaporation rates, we model potential (maximal) SOA production as a function of wind speed, temperature, and oil composition. Existing estimates for the mass of SOA formation following the DWH spill require updated comprehensive yields for aliphatic hydrocarbons that are supported by recent laboratory experiments. The surface-composition of released oil depends greatly on the depth of release, because smaller and more polar hydrocarbons, particularly BTEX compounds, will dissolve in the water column. For light-crude oils, dissolution can increase initial mass fluxes of larger hydrocarbons through Raoult's law effects, and this will also affect observations of SOA in the vicinity of the spill.